Translation of Masasane et al. (JP-A-03-056433)

SPECIFICATION

1. Title of the Invention

Production Method of Dimethyl Ether

2. Claims

1 A method for producing dimethyl ether characterized in that methanol is dehydrated in the presence of a γ-alumina catalyst having a surface area of 210 - 300 m^2/g; a volume of pores with a radius smaller than 300 Å of 0.60 - 0.90 ml/g; and an average pore radius of 50 - 100 Å.

3. Detailed Description of the Invention

The present invention relates to a method for producing dimethyl ether by a dehydration reaction of methanol.

In particular, the present invention relates to an improvement of a catalyst for producing dimethyl ether by dehydration reaction of methanol in vapor phase.

Market demand for dimethyl ether as a propellant for spraying is increasing for replacing chlorofluorocarbons which are becoming an issue of environmental pollution.

[Prior Art]

As for producing dimethyl ether by dehydrating methanol in the presence of an alumina catalyst, for example, there is discussed activity of alumina catalysts having different surface areas in Journal of Colloid and Interface Science, vol. 21, page 349 - 357 (1966).

JP-A-S59-16845 describes a synthetic method of dimethyl ether using a alumina catalyst with large pore radius having an average pore radius of 500 - 1000 nm.

[Subject to Be Solved by the Invention]

By using a γ-alumina catalyst having a surface area up to around 220 m^2/g as mentioned in the above literature, there is obtained an initial activity of the catalyst, for example, such that a methanol conversion of 75 - 80 % and a selectivity of dimethyl ether of 99 % or more, under the conditions of a reaction temperature of 330 °C, a reaction pressure of 10 Kg/cm^2 and a space velocity of 3000 h^{-1}. This initial activity is industrially sufficient. However, upon investigation into changes over time, the activity decreases in one or two months and the methanol conversion decreases to about 65 - 70 %. Therefore, it is generally conducted to recover the methanol conversion by raising the reaction temperature.

However, raising the reaction temperature results in a increase in duty of a electric heater or a combustion furnace which heats a heat medium (externally circulated) for heating a reactor. Also, since hydrocarbons such as methane, ethylene and propylene, carbon monoxide and carbon dioxide are generated as decomposed gases, the selectivity of dimethyl ether decreases and utilization ratio of methanol decreases. This results in a loss of dimethyl ether in purification of dimethyl ether for removing impurities such as hydrocarbons.

The method for producing dimethyl ether using a γ-alumina catalyst having pores with large pore radius as described in JP-A-S59-16845 was found in order to further improve catalyst activity of prior art. However, as reported that when an average pore radius is 350 Å or more, catalyst strength drastically

decreases (Kinetika : Kataliz, 2, No.5, P-859 (1966)), the catalyst with large pore radius is weak in mechanical strength. Thus, the catalyst has defects such that it is necessary to be very careful when handling the catalyst, and that the catalyst easily becomes powder during operation.

As described above, conventional γ-alumina catalysts have defects such as inferior long-term stability.

It is considered that the cause of the defects is coking phenomenon, i.e., carbonaceous substances deposit on the surface of the catalyst and inside the pores during long-term use.

As for the issue of long-term stability of catalyst activity, a γ-alumina catalyst with large pore radius, as the only different property, was found as described in JP-A-S59-16845. However, besides the above mentioned problems, long-term stability of the catalyst activity is uncertain.

Accordingly, an object of the present invention is to provide a method for producing dimethyl ether capable of ensuring stable catalyst activity in the long term, by controlling the properties of the catalyst used for the dehydration reaction of methanol.

[Means for Solving the Subject and Action]

As for the issue of long-term stability of activity of γ-alumina catalysts used for producing dimethyl ether, after intense investigation into the relation between properties of γ-alumina catalysts and long-term stability of the catalyst activity, the inventors have found that a porous γ-alumina catalyst having a specific surface area, pore distribution and average pore radius shows a long-term stability. And after further investigation, the inventors have reached the present invention.

The present invention provides a method for producing dimethyl ether characterized in that methanol is dehydrated in the presence of a γ-alumina catalyst having a surface area of 210 - 300 m^2/g; a volume of pores with a radius smaller than 300 Å of 0.60 - 0.90 ml/g; and an average pore radius of 50 - 100 Å.

Hereinafter, the present invention will be explained in detail.

A porous γ-alumina catalyst used in the present invention is, for example, made according to a method described in JP-A-S49-31597.

The method for producing a porous alumina described in JP-A-S49-31597 is a method such that an amorphous alumina hydrate is heated to 50 °C or more with agitation under a mild alkali condition of pH 8 - 12 to especially generate pseudo-Boehmite having a particle diameter of 80 Å or more, and then the alumina hydrate containing the pseudo-Boehmite is dried and shaped, and further calcined.

The porous γ-alumina catalyst used in the present invention is required to have a surface area of 210 - 300 m^2/g, preferably 230 - 290 m^2/g; a volume of the pores with 300 Å or less in radius of 0.60 - 0.90 ml/g, preferably 0.62 - 0.85 ml/g; and an average pore radius of 50 - 100 Å, preferably 50 - 85 Å.

It is preferred to conduct the dehydration reaction under the conditions of reaction temperature: 200 - 400 °C, preferably 230 - 380 °C; reaction pressure: 1 - 20 Kg/cm^2, preferably 5 - 15 Kg/cm^2; gas hourly space velocity (GHSV): 500 - 10000 h^{-1}, preferably 1000 - 5000 h^{-1}, in order to producing dimethyl ether by dehydrating methanol in the presence of the γ-alumina catalyst in the present invention.

The γ-alumina catalyst according to the present invention is generally used in the form of a sphere or a cylinder, but is not limited to these forms.

Hereinafter, the present invention will be more specifically described with

reference to examples.

Analysis is conducted by gas-chromatography.

Example 1

A hundred (100) ml of porous alumina catalyst shaped in the form of a sphere with a diameter of 3 mm (surface area: 260 m^2/g, volume of the pores with 300 Å or less in radius: 0.7 ml/g, average pore radius: 54 Å) was loaded in a stainless fixed bed reactor with an inner diameter of 20 mm equipped with an electric furnace around its periphery.

Then, at a temperature of the reactor outer periphery of 260 °C, gaseous methanol was supplied at a GHSV of 3000 h^{-1} and a pressure of 10 Kg/cm^2G. The temperature at the inlet of the catalyst layer was 260 °C, and the maximum temperature in the catalyst layer was 325 °C.

As initial results of the reaction, the methanol conversion was 82.6 % and the dimethyl ether selectivity was 99 % or more. A life test for the catalyst was conducted under the above condition, and after six months, the methanol conversion was 74.2 % and the dimethyl ether selectivity was 99 % or more under the same conditions. The results are shown in Table 1.

Example 2

A reaction was conducted in the same manner and using the same apparatus as described in Example 1, except for using a porous γ-alumina catalyst (sphere shape, 3 mm in diameter) having a surface area of 210 m^2/g, a volume of the pores with 300 Å or less in radius of 0.86 ml/g and an average pore radius of 81 Å.

The temperature of the outer periphery of the reactor and the gas

temperature at the inlet of the catalyst layer were both 260 °C during the life test. The results are shown in Table 2.

Example 3

A reaction was conducted in the same manner and using the same apparatus as described in Example 1, except for using a porous γ-alumina catalyst (sphere shape, 3 mm in diameter) having a surface area of 230 m^2/g, a volume of the pores with 300 Å or less in radius of 0.62 ml/g and an average pore radius of 55 Å.

The temperature of the outer periphery of the reactor and the gas temperature at the inlet of the catalyst layer were both 260 °C during the life test. The results are shown in Table 3.

Table 1

Operating Days	Methanol Conversion (%)	Dimethyl ether Selectivity (%)	Ratio to Dimethyl ether (ppm: Vol)		
			Methane	Other Hydrocarbons	$CO+CO_2$
1	82.6	>99	115	1.9	130
90	78.1	>99	100	2.0	125
180	74.2	>99	97	2.0	127

Table 2

Operating Days	Methanol Conversion (%)	Dimethyl ether Selectivity (%)	Ratio to Dimethyl ether (ppm: Vol)		
			Methane	Other Hydrocarbons	$CO+CO_2$
1	81.6	>99	113	1.8	128
90	78.3	>99	101	2.0	126
180	75.1	>99	99	1.7	126

Table 3

Operating Days	Methanol Conversion (%)	Dimethyl ether Selectivity (%)	Ratio to Dimethyl ether (ppm: Vol)		
			Methane	Other Hydrocarbons	$CO+CO_2$
1	80.1	>99	109	1.7	135
90	76.5	>99	108	1.6	130
180	72.3	>99	106	1.5	120

Comparative Example 1

A reaction was conducted in the same manner and using the same apparatus as described in Example 1, except for using a commercially available α-alumina catalyst having a surface area of 175 m^2/g, a volume of the pores with 300 Å or less in radius of 0.50 ml/g and an average pore radius of 57 Å, in the form of a tablet of 1/8 inch X 1/8 inch. The results are shown in Table 4.

Thus, when using the catalyst of prior art which has a small surface area and a small pore volume, there was a tendency that the initial activity drastically decreased in a half - one month. Afterwards, when raising the reaction temperature by 10 °C, it appeared that the catalyst showed relatively stable activity. However, the methanol conversion went down to 70 % or lower in three months. After further raising the temperature of the outer periphery of the reactor by 10 °C, the catalyst activity continued to decrease, and it was necessary to raise the temperature of the outer periphery of the reactor by 10 °C about every month.

Table 4

Operating Days	Reactor outer periphery Temperature (°C)	Methanol Conversion (%)	Dimethyl ether Selectivity (%)	Ratio to Dimethyl ether (ppm: Vol)		
				Methane	Other Hydro-carbons	$CO+CO_2$
1	260	78.1	>99	210	4.5	260
18	260	72.5	>99	205	4.5	268
19	270	77.4	>99	307	4.8	381
104	270	68.0	>99	296	4.7	388
105	280	74.9	>99	411	9.1	510
131	280	69.2	>99	403	8.7	515
132	290	75.1	>99	457	12.0	602
157	290	68.9	>99	440	13.0	631

[Effects of the Invention]

According to the method for producing dimethyl ether of the present invention, by controlling properties of a γ-alumina catalyst used, it is possible to obtain an unconventional long-term stability of the catalyst activity, consequently, by-production of decomposed gases such as hydrocarbons, carbon monoxide and carbon dioxide is suppressed, and accordingly, loss in purification of dimethyl ether decreases. Thus a very excellent industrial method for producing dimethyl ether is provided.